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Estimation of the physical constants of a polydimethylsilane crystal and its evaporated film

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Abstract. The lattice parameters and density of the polydimethylsilane crystal, and the stiffness constants of the film prepared by the evaporation of the source polydimethylsilane powder, have been estimated using the x-ray diffraction technique and the surface acoustic wave, respectively. In the former case, the experimental x-ray diffraction patterns are compared with the theoretical patterns. As a result, it is found that the crystallographic structure of the polydimethylsilane crystal is monoclinic, with the lattice parameters $a = 0.745 \pm 0.001$ nm, $b = 0.724 \pm 0.001$ nm, $c = 0.389 \pm 0.001$ nm and $\gamma = 67.1 \pm 0.1^\circ$. In the latter case, the stiffness constants are estimated from the velocity of the surface acoustic wave propagating along the evaporated film/piezoelectric substrate structure. The values obtained on the assumption that the film is isotropic are $c_{11} = (5.9 \pm 0.9) \times 10^{10}$ N m⁻², $c_{12} = (3.5 \pm 0.9) \times 10^{10}$ N m⁻² and $c_{44} = (1.2 \pm 0.3) \times 10^{10}$ N m⁻².

1. Introduction

Organopolysilanes having one-dimensional silicon backbones are expected to be used for future electronic and optical devices. Polydimethylsilane is the most fundamental material of these. However, only a few papers have reported data for this material. For example, the electronic structure of the polydimethylsilane having an all-*trans* conformation has been calculated by Mintmire (1989). Concerning experimental data, the AT&T group has examined chemically synthesized polydimethylsilane using the x-ray diffraction technique. The reflections observed were indexed as a monoclinic unit cell having dimensions $a = 1.218$ nm, $b = 0.800$ nm, $c = 0.388$ nm and $\gamma = 91^\circ$ (Lovinger *et al* 1991). However, Lovinger *et al* have not reported the packing of the polymer chains. Our group has reported the optical and electrical properties of films prepared by the evaporation of the source polydimethylsilane powder (Furukawa *et al* 1992b, c). Evaporated films were used because there is no good solvent for the polydimethylsilane. This is the reason why the physical properties of polydimethylsilane have not been well examined yet.

In this paper, the physical constants of the polydimethylsilane are estimated using the x-ray diffraction technique and the surface acoustic wave. Fortunately, the evaporated film as well as the source powder material are crystallized; so information about the crystallographic structure can be obtained by x-ray diffraction patterns, as reported by

Lovinger *et al.* The theoretical diffraction pattern is also calculated by assuming the most plausible lattice parameters and the positions of atoms in the unit cell and is compared with the experimental pattern. Thus, the lattice parameters as well as the packing of the chains of the polydimethylsilane crystal can be determined. The density of the polydimethylsilane crystal is also obtained from the resultant crystallographic structure.

On the other hand, the stiffness constants can be obtained by measuring the acoustic wave velocity. Such a measurement is performed for the evaporated film. Because bulk waves cannot be applied to the thin film, the surface acoustic wave propagating along the film/piezoelectric substrate structure is used in this study. The measured surface acoustic wave velocity is compared with the theoretical value, and the stiffness constants of the film are determined.

2. Experimental method and theoretical calculation

2.1. Sample preparation

The source polydimethylsilane powder $[\text{Si}(\text{CH}_3)_2]_n$ with $n \approx 2000$ was chemically synthesized (Furukawa *et al* 1992c). The material film was obtained by evaporating the source powder in a vacuum chamber. First, the source powder and various substrates (single-crystal Si wafer, quartz glass and slide glass) were set on a molybdenum evaporator and a substrate holder, respectively, in the vacuum chamber. Then, the chamber was evacuated to about 10^{-6} Torr using a rotary vacuum pump and a diffusion pump. After evacuation, the substrates were heated to 300–670 K. The powder was then evaporated by applying an AC current of tens of amperes. The thickness of the obtained films was 10–90 μm .

2.2. X-ray diffraction

X-ray diffraction measurements using the θ - 2θ scan mode were performed for both the source powder and the evaporated film. The substrate used was a single-crystal Si(100) wafer, because it does not cause strong diffraction in a 2θ range of less than 60° . The acceleration voltage and the beam current for the x-ray measurements were 40 kV and 80 mA, respectively.

The x-ray diffraction pattern thus obtained was compared with the theoretical pattern. In the calculation, the lattice parameters were first determined from the diffraction peak positions, i.e. the values of 2θ . The positions of the atoms were then determined by considering the previously reported conformation of the silicon backbone and reasonable packing of the chains. Next, the structure factor was evaluated for each diffraction index. All the atoms including hydrogen atoms were considered in this study. The Si–Si–Si and the C–Si–C bond angles were selected to be 111.7° and 108.0° , respectively (Mintmire 1989), and the H–C–H bond angle was assumed to be tetrahedral. The number of the equivalent lattice planes as well as the Debye–Waller factor were also taken into account. The shape of the diffraction peak was assumed to be a Gaussian type, and an appropriate half-width for it was also assumed in order to compare the theoretical with the experimental pattern.

2.3. Measurement of elastic properties

The elastic properties of the evaporated film were measured using the surface acoustic wave. A 36° -rotated Y -cut and X -propagation (36° rotated Y - X) LiNbO_3 substrate was used as the piezoelectric material (Furukawa *et al* 1992a). The surface acoustic wave was excited and received by a pair of inter-digital transducers, which were fabricated by

evaporating an aluminium thin film onto the LiNbO_3 substrate, and using a photo-etching technique. The frequency of the surface acoustic wave excited by the transducer was about 30 MHz. After fabricating the inter-digital transducers, the material film was evaporated in the vacuum chamber. A schematic diagram of the fabricated specimen is shown in figure 1. The velocity and the propagation loss of the surface acoustic wave were measured using a conventional oscillator and a vector voltmeter. The details of the procedure have been described elsewhere (Nomura *et al* 1992).

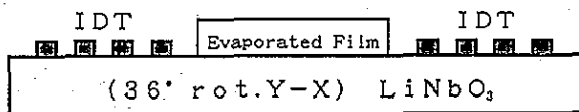


Figure 1. Schematic diagram of the fabricated layered structure for the elastic property measurement. The surface acoustic wave is excited and received by a pair of inter-digital transducers (IDTs).

Surface acoustic waves consist of both a longitudinal and a transverse component. Therefore, the experimental data should be compared with the theoretical data in order to estimate the stiffness constants of the film. Our group has already developed a computer program to analyse the leaky surface acoustic wave propagating along the liquid/layered substrate structure (Furukawa *et al* 1991); so the theoretical calculation was performed for a water/evaporated film/(36° rotated $Y-X$) LiNbO_3 configuration. The corresponding experiment was carried out, and the result was compared with the theoretical data. In the calculation, the physical constants listed in the book written by Auld (1973) were used for LiNbO_3 , and those described in our previous paper (Furukawa *et al* 1991) were used for water. Concerning the density of the evaporated film, its value was assumed to be 98% of that of the crystal (the reason will be explained later). The density of the polydimethylsilane crystal can be deduced from the crystallographic structure obtained. The stiffness constants of the evaporated film were selected to fit the experimental data.

3. Results and discussion

3.1. X-ray diffraction patterns of source polydimethylsilane powder and its evaporated film

Figures 2(a) and 2(b) show the x-ray diffraction patterns for the source polydimethylsilane powder and the evaporated film, respectively. In figure 2(a), there appear four large diffraction peaks at $2\theta = 13.3^\circ, 14.5^\circ, 26.3^\circ$ and 27.2° , which correspond to lattice spacings of 0.667 nm, 0.612 nm, 0.338 nm and 0.328 nm, respectively. In figure 2(b), the strengths of the two right-hand peaks become very small, and there appear three large peaks in the range $2\theta < 16^\circ$. In the optical absorption spectra, a sharp peak was observed at 300 nm for both the source polydimethylsilane powder and the evaporated film (Furukawa *et al* 1992b, c). This indicates that the evaporated film also contains a number of one-dimensional silicon backbones. Therefore, the change in the diffraction patterns from figure 2(a) to figure 2(b) cannot be explained by the change in the unit cell or the considerable reduction in molecular weight but can be explained by the highly oriented character of the one-dimensional silicon backbones in the evaporated film. In addition to these large diffraction peaks, many small peaks are also observed in figures 2(a) and 2(b).

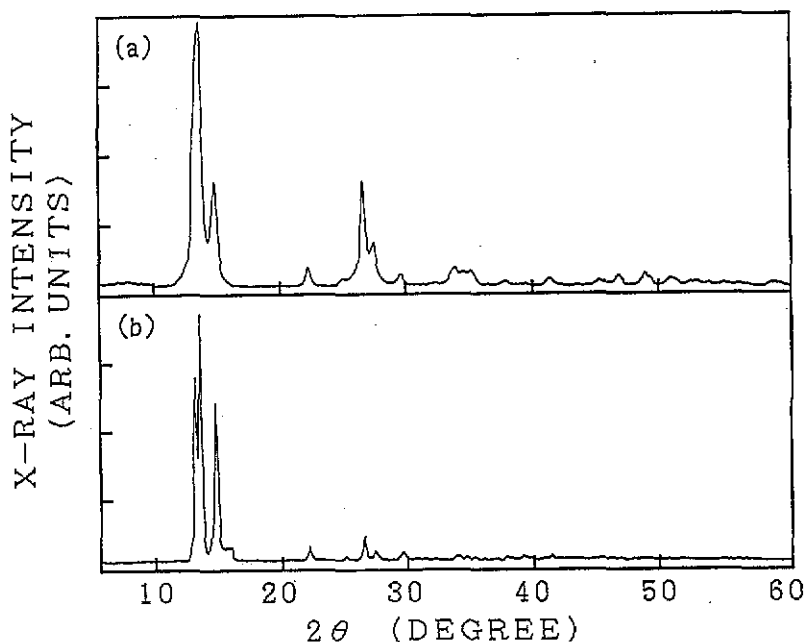


Figure 2. X-ray diffraction patterns for (a) the source polydimethylsilane powder and (b) the evaporated film. The latter film was prepared at 450 K.

3.2. Determination of the crystallographic structure of the polydimethylsilane crystal

Because a large polydimethylsilane single crystal cannot be obtained, we tried to determine the crystallographic structure of the polydimethylsilane crystal from the experimental and theoretical diffraction patterns. That is, the theoretical diffraction pattern of the powdered polydimethylsilane polycrystal was calculated by assuming the unit cell and the positions of the atoms, and the result was compared with the experimental data. In order to select the most plausible lattice parameters, it was assumed that the three large diffraction peaks appearing in figure 2(b) correspond to the three lattice spacings, which are determined by the triangle (characterized by a , b and $a - b$) perpendicular to the c axis (direction of the chains; see later) in a monoclinic unit cell. This assumption is quite reasonable, considering the following fact: that is, the uniaxially oriented thin film of polydimethylsilane has an all-*trans* conformation (Lovinger *et al* 1991). In that case, the diffraction peaks, related to the *trans* period (i.e. (hkl) $l \neq 0$), do not appear on the small-angle side, because the *trans* period (0.389 nm) is relatively small. It was also assumed that the direction of the c axis coincides with that of the silicon backbone, which has an all-*trans* conformation. This corresponds to the highly oriented character of the evaporated film, in which the direction of the one-dimensional silicon backbone is parallel to the substrate surface. From this assumption, the most plausible stack of the chains can be determined as the inset of figure 3. The lattice parameters are determined to be $a = 0.745 \pm 0.001$ nm, $b = 0.724 \pm 0.001$ nm, $c = 0.389 \pm 0.001$ nm and $\gamma = 67.1 \pm 0.1^\circ$. These errors are estimated from the experimental error of the 2θ -values. The ordered stack of the chains is due to the van der Waals force. The magnitudes of a and b are quite reasonable, because the van der Waals radius of the CH_3 group is 0.20–0.23 nm. Figure 3 shows the theoretical diffraction pattern calculated using the unit cell thus obtained. This pattern is for the powdered polycrystal or the

source polydimethylsilane powder. It should be noted that the pattern in figure 3 is in good agreement with that in figure 2(a). This strongly supports the above-stated lattice parameters and the packing of the chains. The size of the unit cell reported by Lovinger *et al* is twice that of the present unit cell. Therefore, their unit cell is not primitive.

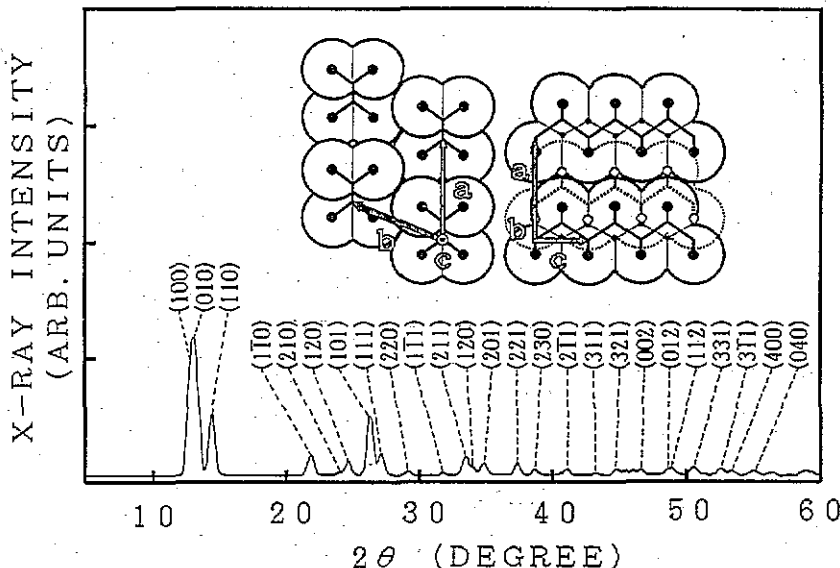


Figure 3. Theoretical x-ray diffraction pattern for the powdered polydimethylsilane crystal. The inset shows the crystallographic structure of the polydimethylsilane crystal. The primitive translation vectors are indicated by a , b and c . The zigzag lines and the circles indicate the silicon backbone and the van der Waals radius of the CH_3 group, respectively.

The difference between the diffraction patterns of the small-angle doublet in figure 2(b) and the broad single peak in figure 2(a) will be discussed as follows: that is, the small-angle broad peak in figure 2(a) consists of two peaks. This is because there exists a shoulder on the small-angle side (see the large left-hand peak in figure 2(a)). This is consistent with the present assignment (see the indexing shown in figure 3) as well as the previous assignment (Lovinger *et al* 1991). As stated in the previous paragraph, the difference between the diffraction patterns in figures 2(a) and 2(b) can be explained by the highly oriented character of the evaporated film. In that case, it is plausible that the shape and the intensity of the diffraction peaks are changed from those of almost isotropic material, i.e. the source powder material. Concerning the difference between the half-widths in the two figures, that of the evaporated film may become smaller because of an annealing effect during the deposition.

3.3. Elastic properties of the evaporated film

It is quite difficult for us to measure the elastic properties of the source polydimethylsilane powder. Therefore, the elastic properties of the film evaporated onto a (36° rotated Y - X) LiNbO_3 substrate were measured using the surface acoustic wave propagating along this structure. As stated in the previous section, the surface acoustic wave consists of both the longitudinal and the transverse components. Moreover, the magnitude of the particle

displacement relevant to the surface wave propagation changes along the surface normal direction. Therefore, the experimental result should be compared with the theoretical result. Concerning the theoretical calculation, we have used the computer program to analyse the leaky surface acoustic wave propagating along the water/thin film/piezoelectric substrate structure (see the previous section). In this case, the surface acoustic wave becomes leaky because of the water loading. Therefore, the experiment was also performed for the water/evaporated film/(36° rotated $Y-X$) LiNbO₃ configuration.

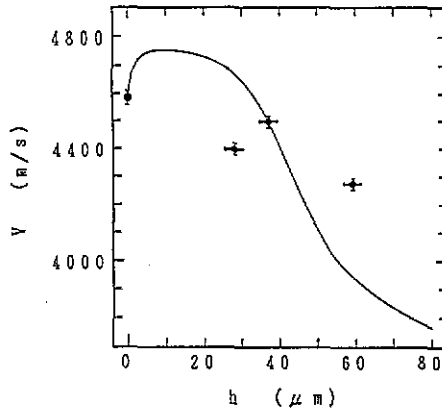


Figure 4. Surface acoustic wave velocity V versus film thickness h , where the frequency is kept constant at 30 MHz: —, theoretical results; ●, experimental results. The substrate temperature during the deposition was 300 K.

Figure 4 shows the relation between the surface acoustic wave velocity and film thickness thus obtained. The full curve and the full circles indicate the theoretical and the experimental results, respectively. The error bars, i.e. Δh and ΔV , are caused by the surface roughness and the ambiguity of the propagation distance, respectively. The acoustic wave velocity is mainly determined by the density and the stiffness constants of the materials. From the crystallographic structure obtained for the polydimethylsilane crystal, the density was calculated to be $996 \pm 5 \text{ kg m}^{-3}$. In the computer simulation, the density of the evaporated film was assumed to be 98% of that of the crystal. The density of the hydrogenated amorphous silicon (a-Si:H), whose hydrogen content was 24 at.%, was reported to be 95% of that of the single-crystal silicon (Brodsky *et al* 1977). The stoichiometry of the present evaporated material is considered to be not very different from that of the source polydimethylsilane. However, the film should contain some grain boundaries and defects. Therefore, a value of 98% of the density of the crystal was selected, although the present material is different from a-Si:H. In order to reduce the number of parameters, the evaporated film was assumed to be isotropic, although the direction of the silicon backbone in the film was parallel to the substrate surface (the film evaporated on LiNbO₃ showed an x-ray diffraction pattern similar to figure 2(b)). Moreover, the ratio c_{11}/c_{44} of the stiffness constants was assumed to be the same as that of polystyrene (Auld 1973). Thus, the number of parameters becomes only one. That parameter, i.e. one of the Lamé constants, was changed and determined to fit the experimental data (see figure 4). The stiffness constants determined are $c_{11} = (5.9 \pm 0.9) \times 10^{10} \text{ N m}^{-2}$, $c_{12} = (3.5 \pm 0.9) \times 10^{10} \text{ N m}^{-2}$ and $c_{44} = (1.2 \pm 0.3) \times 10^{10} \text{ N m}^{-2}$. The errors are estimated by fitting the theoretical curve to the right-hand side ($h = 60 \mu\text{m}$) and the left-hand side ($h = 28 \mu\text{m}$) of the plot

in figure 4. By considering the stiffness constants of other various polymer materials (Auld 1973), the potential errors introduced by the assumption that the films are isotropic are roughly estimated. As a result, the errors are estimated to be a few times larger for c_{11} and c_{12} , and several times larger for c_{44} , than the present errors.

Table 1. Physical constants obtained. The lattice parameters and the density are for the polydimethylsilane crystal, and the stiffness constants are for the evaporated film.

Lattice parameters (monoclinic)	
a	0.745 ± 0.001 nm
b	0.724 ± 0.001 nm
c	0.389 ± 0.001 nm
γ	$67.1 \pm 0.1^\circ$
Density	
ρ	996 ± 5 kg m ⁻³
Stiffness constants (evaporated film)	
c_{11}	$(5.9 \pm 0.9) \times 10^{10}$ N m ⁻²
c_{12}	$(3.5 \pm 0.9) \times 10^{10}$ N m ⁻²
c_{44}	$(1.2 \pm 0.3) \times 10^{10}$ N m ⁻²

4. Summary and conclusion

The physical constants of a polydimethylsilane crystal and its evaporated film were estimated using x-ray diffraction and the surface acoustic wave. The values obtained were summarized in table 1. The lattice parameters and the density are for the polydimethylsilane crystal, and the stiffness constants are for the evaporated film. The former values are considered to be extremely reliable, because the theoretical diffraction pattern is in good agreement with the experimental pattern. Moreover, the distance between the chains as well as the stack shown in the inset of figure 3 are quite reasonable. On the other hand, the latter values are roughly estimated using some assumptions. However, it is suggested that the stiffness constants of the polysilane are larger than those of conventional polymers. This is because polysilane has one-dimensional silicon (not carbon) backbones.

Acknowledgments

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